Characterization of rare-earth aluminum oxynitrides synthesized by carboreduction and nitridation

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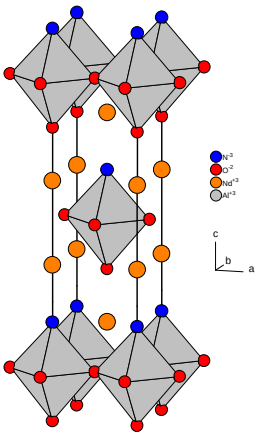
Background

Over the recent years, a great interest has been shown for multinary oxynitrides containing main group elements especially in the fields of phosphors or visible-light driven photocatalysts. However if a tremendous work has been done on nitridosilicates and nitridoalumonisilicates based materials, very little is know about multinary (oxy)nitride systems based on aluminum (R_2AlO_3N, $RAl_{11}O_{12}N$), gallium (La_2GaN_3) or phosphorous (Zn_2PO_3N). A large part of our research is then devoted to the preparation of new materials among those systems by exploring less-common synthesis routes than the usual solid state reaction or the ammonia flow-based nitridation. As a first step of the present work, we have successfully reinvestigated the preparation of the R_2AlO_3N oxynitrides (R = Nd and Sm) using the carboreduction and nitridation process (CRN).

Structure…



Nd_2AlO_3N

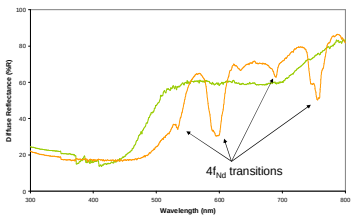
2D-perovskite structure related to the K_2NiF_4 type

S.G. = I4/mm
a = 3.7046 Å
c = 12.5301 Å
V = 171.96 Å^3

R. Marchand et al. – Rev. Chim. Minér. 19 (1982) p684

Optical properties…

Nd_2AlO_3N → orange powder
Sm_2AlO_3N → greenish yellow powder



λ_{Sm} ~ 480 nm
⇨ Yellow

λ_{Nd} ~ 530 nm
⇨ Orange

Thermal analyses…

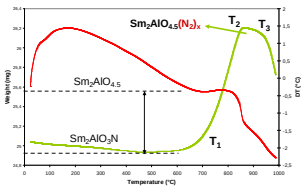
Oxidation under air starts ~ 600°C

Sm_2AlO_3N → $Sm_4Al_2O_9$ + "$SmAlO_3$" + "Sm_2O_3"

T_1 → T_2 : Oxidation with N_2 retention

T_2 → T_3 : "Intermediate phase"

T_3 → : Oxide formation with N_2 release



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Synthesis routes…

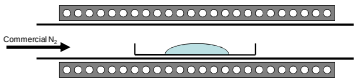
Previous synthesis : mixture of Nd_2O_3 or Sm_2O_3 and AlN sealed under N_2 in nickel tubing and fired at 1350°C with repeated heating.

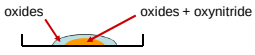
Long reaction process (~ 6 x 24h)
Very difficult to obtain pure samples → $RAlO_3$ and R_2O_3 minor phases

Carboreduction & nitridation (CRN):

$2\ Sm_2O_3 + Al_2O_3 + 3\ C + N_2 \rightarrow 2\ Sm_2AlO_3N + 3\ CO$ T = 1250°C

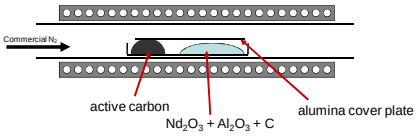
Regular apparatus

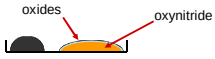




reoxidation during synthesis

"Oxygen trap" apparatus





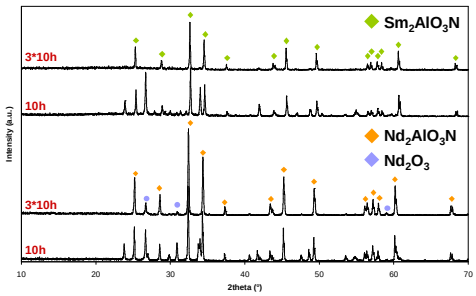
oxides formation efficiently reduced

X-Ray Diffraction…

⇨ Sm_2AlO_3N can be obtained as a nearly pure sample after only 3 heating at 1250°C

⇨ In the same conditions, a Nd_2O_3 impurity phase still be present along with Nd_2AlO_3N

little oxidation remains



Conclusion…

- Carboreduction & Nitridation (CRN) is a convenient way to prepare aluminum based oxynitrides with interesting optical properties and good thermal stability under air.
- Apparatus will be upgraded with a nitrogen gas purification system (moisture and oxygen traps, hot titanium wire) to avoid reoxidation of the samples.
- Other systems are under investigation such as $A_{2-x}R_xAlO_{4-x}N_x$ solid solution with A = Alkaline earth and R = Rare earth.